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Formation of Porous Ceramics Using Cullet and Biological Waste of Water Purification

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Abstract:

Porous ceramics (bricks) was obtained using red clay, milled fusible cullet, and biowaste in the temperature range 950–1000 °C. The high content of water in biowaste eliminates the necessity of introducing water in soft mud forming of bricks. The porosity, water absorption capacity, and mechanical properties of the prepared ceramics depend on content of milled cullet and sintering temperature.

Keywords: Red clay, Cullet, Biowaste, Porous ceramics

1. Introduction

At present, the problem of protection of the environment from industrial and domestic waste acquires particular importance. This is why different technologies for neutralization and utilization of large-scale wastes are being developed. One more ecological problem of comparable importance is the reduction of water consumption at manufacturing enterprises. The third important problem that confronts industrial engineers is the reduction of the product cost. By virtue of the foregoing, it is interesting to develop a technology that meets all these requirements and provides large-scale use of developed products.

Among contaminating solid wastes is cullet, particularly cullet of glass containers of different composition. A part of cullet is used in the manufacture of glass and building materials, but a large part of cullet has not find application.

Another source of large-scale waste is waste of biological purification of water (by aerobic and anaerobic bacteria), which predominantly arrive to dumps from water treatment plants. Only the insignificant part of such waste is used in agriculture. As a rule, this biowaste are thrown out. It is important to note that biowaste contain a large amount of water. This is why they can be used in technologies that require the introduction of service water for obtaining a plastic easily formed semiproduct.

Thus, the choice of cullet and biowaste as raw materials dictates the choice of the basic component in a technology. In particular, as a basic component, one can use red clay, which is extensively used in the production of bricks. Since biowaste must burn out, it can be assumed that porous ceramic will form. On the other hand, the presence of water in biowaste must provide a decrease in the water consumption in the production of green bricks.

Thus, the aim of the work is to develop the manufacturing process of strong porous ceramic using red clay, fusible cullet, and biowaste. The manufacturing process of the plastic semiproduct must be realized without introducing free water. Let's note that the porous
ceramics finds wide application in various areas of techniques [1-3]. However, down to present time even such traditional technologies as reception of bricks [4-11] are constantly modified.

2. Preparation of Specimens and Experimental Procedure

In the work, we used fusible red clay with a narrow sintering temperature range (950–1050 °C). Its composition is presented in Tab. I. As an additive to clay, milled cullet of bottles was introduced (see Tab. I). Two types of milled cullet, namely cullet with a particle size < 595 µm (which passed through a 30 mesh screen) and cullet with a particle size < 250 µm (which passed through a 60 mesh screen) were used. The melting point of this type of glass ranges from 650 to 750 °C. Specimens were made by the standard soft mud forming method [4-5]. Two types of bricks, namely red clay–milled cullet–water (specimens A) and red clay–milled cullet–biowaste (specimens B) were obtained. The content of milled cullet ranged from 10 to 80 wt. %. The biomass content in briquettes was ~ 30 vol. % concerning total volume of a mixture clay-glass. Laboratory 80×15×15 mm specimens were sintered at 800, 900, 950, and 1000 °C for 2 h. In soft mud forming of samples B, water was not added.

<table>
<thead>
<tr>
<th>Components of the prepared mixtures</th>
<th>Content of oxides, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>Clay</td>
<td>56</td>
</tr>
<tr>
<td>Glass</td>
<td>70.7</td>
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</table>

An X-ray analysis of the specimens was performed using a Siemens D-500 diffractometer in Cu Kα radiation. Scanning electron microscopy studies were carried out with an HU-200F unit. Water absorption (W) by ceramics was defined by standard method in boiling water during 3 h by a standard technique [12, 13]. The given W corresponds to average value obtained on 3 samples. Compression and bending tests were carried out by standard techniques. The mechanical properties (microhardness) were determined with a LECO 300AT microhardness tester and a Vickers indenter under a load of 10 N with a holding time of 15 s. On each specimen were performed ten measurements and then were averaged. Particles size was measured on a laser particles sized in wet dispersing regimen with the using of continuous stirring and ultrasound application (Analysette 22 COMPACT unit).

3. Experimental Results and Discussion

3.1. Characterization of initial components

A crystallogram of red clay shows that it has a complex composition and contains montmorillonite, kaolin, dickite, quarts, crystobalite, and feldspar (Fig. 1 a).

Particle size distributions of clay and glass powder are shown in Fig. 2. The use of ultrasound treatment showed that clay particles are present in the form of aggregates.

3.2. Ceramics on base clay–milled cullet–water (specimens A)

The sintering of specimens at 950 °C is accompanied by the decomposition of clay
minerals. In crystallograms, lines of different types of clays disappear, which agree with data of [4, 5]. The intensities of lines of feldspar decrease, and lines of secondary feldspars appear. In all X-ray diffraction patterns, lines of cristobalite and quartz are present. For the sintered specimens with a large glass content, halo is observed (Fig. 1 b, c).

After sintering at 1000 °C, in X-ray diffraction patterns, lines of low-temperature aluminum silicate of different composition (metakaolin and sillimanite) appear. However, their intensities are insignificant (Fig. 1 d, e). As for specimens with a large glass content and sintered at 950 °C, in X-ray diffraction patterns of specimens with a large glass content and sintered at 1000 °C, halo is observed. In these specimens, main crystalline phases are feldspars.

The obtained results show that the glass melt and decomposition products of clay

![Image](image-url)
minerals interact with the formation of new phases [14, 15]. A part of the sintered material is in the X-ray amorphous state (in the form of a glass phase).

Fig. 2. Particle size distributions for clay (a) before and (b) after using ultrasound and milled cullet after screen analysis (60 mesh screen) (c).

Fig. 3. Dependences of the water absorption capacity of bricks on the sintering temperature of red clay–milled cullet mixtures. (a) 90 wt. % clay–10 wt. % milled cullet; (b) 80 wt. % clay–20 wt. % milled cullet; (c) 50 wt. % clay–50 wt. % milled cullet; (d) 20 wt. % clay–80 wt. % milled cullet sintered for 2 h. $d_g < 250$ µm.

The investigation of the process of water absorption showed that the absorption capacity of sintered ceramic decreases as the sintering temperature (Fig. 3) and the glass
content in the initial mixture (Fig. 4) increase. Specimens with a large glass content sintered even at a temperature of 850 to 950 contained not larger than 5% of absorbed water. The strength of the ceramic increases as the glass content in it increases (Fig. 5). Note that the compression strength and bending strength of the ceramic increase substantially as the sintering time increases.

![Fig. 4. Dependent of the water absorption capacity on the glass content in red clay–milled cullet mixtures for bricks sintered at 950 °C for 120 min.](image)

![Fig. 5. Dependent of the compressive strength (a) and the bending strength (b) on the content of glass in red clay–milled cullet mixtures for bricks sintered at 950 °C (1) and 1000 °C (2) for 2 h.](image)

3.3. Ceramics on base clay–milled cullet–biowaste (specimens B)

Since in the synthesis of porous ceramic, we used biowaste, the process of its thermodestruction was investigated (Fig. 6). The largest loss of weight is observed in the temperature range 200–300 °C at the expense of release of water vapor and carbonic acid gas. The content of the ash residue does not exceed 3 %. It contains an insignificant amount of oxides. The chemical analysis of initial biowaste is presented on Tab. 2.
Tab. II. The chemical analysis of initial biowaste

<table>
<thead>
<tr>
<th>Components</th>
<th>Content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic material</td>
<td>88.50</td>
</tr>
<tr>
<td>clay</td>
<td>7.9</td>
</tr>
<tr>
<td>CaO</td>
<td>1.28·10^{-1}</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.67·10^{-2}</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>4.3·10^{-4}</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>2.46·10^{-4}</td>
</tr>
<tr>
<td>MgO</td>
<td>1.39·10^{-3}</td>
</tr>
<tr>
<td>Zn</td>
<td>7.2·10^{-4}</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.8·10^{-4}</td>
</tr>
<tr>
<td>Cu</td>
<td>2.7·10^{-4}</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.9·10^{-4}</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1·10^{-6}</td>
</tr>
</tbody>
</table>

Fig. 6. Character of thermodestruction of biowaste of water treatment.

3. 3. 1. XRD, electron microscopy, and electron probe microanalysis

According to the XRD data, the structural phase transformations occurring in specimens of this serried in sintering do not differ from those for the clay–milled cullet–water specimens (see Fig. 1).

Fig. 7. Micrograph of a fracture of the ceramic (a, b) obtained from the 90 wt. % clay–10 wt. % milled cullet mixture and sintered at 950 °C for 2 h. d₈ < 595 μm. (b) corresponds to place 2.
In a micrograph (Fig. 7), we can see that the ceramic with the smallest (10 wt.%) glass content sintered at 950 °C is a highly porous inhomogeneous material, in which three types of regions are present. These are regions where aluminum silicates (decomposition products of clay minerals) are concentrated (region 1 in Fig. 7a and Fig. 8, 1), regions of the "vitreous" phase (region 2 in Fig. 7a, b), containing not only the elements characteristic of aluminum silicates, but also elements present in milled glass (see Fig. 8, 2), and regions where silica is concentrated (region 3 in Fig. 7a and Fig. 8, 3).

Fig. 7. Contents of elements at places marked by digits 1, 2, and 3 in Fig. 7.

With increase in the sintering temperature and in the content of milled glass, the morphology of fractures changes, the size of vitreous regions increases (see Figs. 9 and 10), and the porosity of specimens decreases.

Fig. 8. Micrographs of fractures of the ceramic obtained from the 90 wt. % clay–10 wt. % milled cullet mixture and sintered at temperatures of 950 °C (a) and 1000 °C (b) for 2 h. d₅₉ < 595 µm.
The electron probe microanalysis results show that the elemental composition of the “vitreous phase”, particularly in the ceramic obtained at 1000 °C, is not constant. In different zones of the specimen, different sets of elements are present, and their contents differ (Fig. 11). Nevertheless, the elemental composition data enable us to distinguish regions with a large content of silica (Fig. 11 a, b), aluminum silicate (Fig. 11 c), multicomponent glass and/or feldspars (Fig. 11 d, i). It is assumed that this distribution of elements is due to the inhomogeneity of the initial clay–milled glass mixture.

It should be noted that, in the ceramic obtained from the mixture with a large content of milled glass and sintered at 950 °C, at places of localization of the "glass phase", carbon was detected (Fig. 12). This is explained by the fact that the melt of the "glass phase" and the eutectic melt of silica and feldspars of certain viscosity hinder the penetration of oxygen of air into pores, which, in turn, hinders the burning of products of thermodestruction of biomass. However, in the ceramic sintered at 1000 °C, at which the viscosity of the melt decreases and the melt is distributed more homogeneously over the volume, carbon was not detected. A substantial difference in the formation of a porous body with using of glass powders with a particle size of 595 and 250 µm was not detected. This indicates that, in the used temperature
range of sintering 950–1000 °C, the glass phase is already in the liquid state and has a small viscosity.

Fig. 11. Contents of elements at different places of a specimen obtained from the 90 wt. % clay–10 wt. % milled cullet mixture and sintered at 1000 °C for 2 h. $d_g < 250 \mu$m.

Fig. 12. The content of elements at different places of a specimen obtained from the 54 wt. % clay–46 wt. % milled cullet mixture and sintered at 950 °C for 2 h. $d_g < 250 \mu$m.
3. 3. 4. Results of investigation of water absorption capacity of ceramic on base clay–glass–biomass

The performed electron microscopy studies showed that the sintering of the specimens obtained from mixtures containing biomass is accompanied by the formation of open and closed pores in the ceramic even in the case of large amounts of glass powder in the mixtures and high sintering temperatures.

Fig. 13. Dependences of the water absorption capacity on the sintering temperature of specimens prepared from red clay–milled cullet–biomass mixtures: (a) 54 wt. % clay–46 wt. % glass; (b) 80 wt. % clay–20 wt. % glass; (c) 90 wt. % clay–10 wt. % glass and sintered for 2 h. $d_g \sim 250 \mu$m.

Fig. 14. Dependences of the water absorption capacity on the content of glass in red clay–milled cullet–biomass mixtures sintered at (a) 950 °C and (b) 1000 °C for 2 h. $d_g \sim 250 \mu$m.
Fig. 15. Dependences of the water absorption capacity on the sintering temperature of specimens made from the red clay–milled cullet–biomass mixtures: (a) 54 wt. % clay–46 wt. % glass; (b) 80 wt. % clay–20 wt. % glass; (c) 90 wt. % clay–10 wt. % glass sintered for 2 h. \(d_g \sim 595 \, \mu m\).

From the results of the investigation of the water absorption capacity of these specimens (Figs. 13-17) it can be concluded that the open porosity decreases as the sintering temperature and the content of glass powder in the initial mixtures increase. The difference in the water absorption capacity of specimens made using different fractions of glass powder (see Fig. 17) can be explained by the fact that the glass powder with a smaller particle size transforms faster into the liquid state and the glass melt takes a more active part in the formation of a new multicomponent melt. This process must be accompanied by the more intensive evolution of gas. The XRD data that indicate the formation of new feldspars agree with this assumption.

Fig. 16. Dependences of the water absorption capacity on the glass content in red clay–milled cullet–biomass mixtures for specimens sintered at (a) 950 °C and (b) 1000 °C for 2 h. \(d_g \sim 595 \, \mu m\).
Fig. 17. Dependences of the water absorption capacity on the size of glass powder particles for specimens obtained from red clay–milled cullet mixtures with different glass contents and sintered at (a) 950 °C and (b) 1000 °C for 2 h. (1) \( d_g < 595 \mu m \); (2) \( d_g \sim 250 \mu m \).

Comparing the values of the water absorption capacity of these specimens and ceramic obtained on the base of the clay–glass–water mixtures (see Figs. 3, 4 and 13-17) and sintered under the same manufacturing conditions, it can be concluded the burning-out of biomass increases the porosity of the ceramic.

5. Mechanical properties of the synthesized porous ceramics

The results of the fracture toughness investigation indicate that the cracking process depends on content of glass powder in the initial mixtures, sintering temperature, and particle size of glass powder. In Fig. 18 a, we can see that at use of a coarse-grained glass powder \( (d_g \leq 595 \mu m) \) with increase of its content, the strength of the ceramic increases. However, in the case of using more disperse glass powder (Fig. 18 b), this tendency is retained only in “low-temperature” sintering, and as the sintering increases, a decrease in the strength of specimens is observed, which is more clearly seen in Fig. 19. Taking into account the data of XRD, electron microscopy, electron beam microanalysis, and the study of the water absorption capacity, we can assume that, in sintering at a temperature of 1000 °C, the interaction of the components of the mixtures is substantially intensified, and the content of the newly formed glass phase increases as the glass content in the mixtures increases. As a result, mechanical stresses, which may lead to decreases in the strength properties, arise on interfaces. In Fig. 10, we can see such a fracture.

Fig. 18. Dependences of the fracture toughness on the content of milled cullet in initial mixtures. For (a) \( d_g < 595 \mu m \) and (b) \( d_g \sim 250 \mu m \). (1) \( T_s = 950 \) °C, (2) \( T_s = 1000 \) °C. \( t_s = 2 \) h.
Fig. 19. Dependence of the fracture toughness on the content of milled cullet in initial mixtures. For (a) $T_s = 950 \, ^\circ C$, (b) $T_s = 1000 \, ^\circ C$. $t_s = 2 \, h$. (1) $d_g < 259 \, \mu m$; (2) $d_g < 595 \, \mu m$.

Thus, the performed investigations showed that the introduction of biomass into the composition red clay–milled cullet leads to the formation of porous ceramics. In this case, the porosity of sintered specimens changes depending on the amount of the introduced milled cullet and sintering temperature. With increase in the sintering temperature, the homogeneity of distribution of the glass phase over the body of a specimen and its strength properties increase. Taking into account the formation of the eutectic in the silica–feldspar system at a temperature of about 990 °C [15, 16], it can be assumed that the formation of the glass melt at a temperature of about 800 °C provides conditions for the formation of a lower-temperature eutectic with a large content of the melt of smaller viscosity.

The varying elemental composition at different places of specimens is due to not only the inhomogeneity of the distribution of the components in the mixture, but also the development of the processes of interaction between the low-temperature melts of cullet, formed aluminum silicates, silica and feldspars present in the initial clay. This is indicated by changes in the intensities of peaks assigned to silica and feldspar in the initial clay and the appearance of lines assigned to new crystalline feldspar-type phases in X-ray diffraction patterns (see Fig. 1).

4. Conclusions

It was established that substantial amounts (to 50 wt. %) of fusible milled cullet can be added to red clay. Glass is a binding agent for silica-alumina particles at low sintering temperatures. Therefore, varying the glass content in mixtures it is possible to improve the strength properties of sintered bricks.

The presence of water in biowaste makes it possible to carry out soft mud forming of bricks without introducing additional water into clay.

Due to the thermodestruction of biowaste and the release of water vapor and carbonic gas, a porous structure of bricks forms.

The obtained results show that the use of biological waste of water purification and cullet is promising for the large-scale synthesis of porous bricks.

References

17. E. F. Osborn, A. Muan, in: E.M. Levin, C.R. Robbins, H.F. Mc Murdie, Phase diagrams for ceramists, USA, Columbus, 1964, Fig. 712.

Садржај: Порозне керамике (цигле) добијене су употребом црвене глине, млевених отпадака од топљеног стакла и биоотпадака на температурама од 950 до 1000 °C. Висок садржај воде у биоотпадцима елиминише потребу за водом током формирања цигле из течног муља. Порозност, капацитет за абсорцију воде и механички својства добијене керамике зависе од садржаја отпадака од стакла и температуре синтеровања.

Кључне речи: Црвена глина, отпади од стакла, биоотпади, порозна керамика